

Ethanol electrooxidation on activated graphite supported platinum-nickel in alkaline medium

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Abstract In this study, activated graphite-supported platinum (Pt/C), nickel (Ni/C) and platinum-nickel (Pt–Ni/C) were prepared by electrodeposition technique using solutions containing hexachloroplatinic acid and/or nickel sulphate. Ethanol electrooxidation was investigated on Pt/C, Ni/C and Pt–Ni/C electrocatalysts by cyclic voltammetry and chronoamperometry in aqueous alkaline solution containing 1.0 M NaOH and 2.0 M C₂H₅OH. The electrocatalytic activities and stabilities of the electrocatalysts were discussed. The results showed that ethanol is oxidized anodically on Ni/C. This reaction occurred simultaneously with the anodic oxidation of nickel hydroxide (Ni(OH)₂) into nickel oxy-hydroxide (NiOOH). It is also found that Pt–Ni/C electrocatalytic characteristics were better than Pt/C. The Pt–Ni/C electrocatalyst exhibited excellent activity and enhanced stability than Pt/C. It seems that Pt–Ni/C is a promising electrocatalyst toward ethanol electrooxidation in alkaline medium for fuel cells applications.

Keywords Fuel cells · Electrodeposition · Platinum-nickel · Ethanol electrooxidation · Cyclic voltammetry

1 Introduction

In the past two decades, direct alcohol fuel cells (DAFCs) which operate directly on liquid fuels have been studied extensively owing to their low operating temperature (below 100 °C) and the fast startup for applications such as portable devices, stationary power sources and electric vehicle technology [1–3]. Amongst the different types of DAFCs, those using methanol have attracted the greatest attention. Because methanol is readily available and is structurally simple, it is a promising source of electrochemical activity [4–6]. Nevertheless, two significant barriers may restrain the development of practical methanol oxidation fuel cells, namely the low activity of anode catalysts and the methanol crossover to the cathode [2]. Recently, ethanol has gained a particular attention because it is considered as a green fuel in such a way that it can be produced from renewable sources [7]. It is also less toxic than methanol [8]. Moreover, ethanol can serve as a model compound since it is the smallest oxygenated organic molecule involving a C–C bond that should be broken to achieve total oxidation [7–10].

As far as carbon-supported platinum is concerned, it is commonly used as anode electrocatalyst in direct ethanol fuel cell (DEFC) at low temperature [11–13]. Nonetheless, adsorbed CO resulting from ethanol electrooxidation reaction poisons the electrode and drastically reduces the activity of pure platinum [14]. Moreover, it has a limited ability for breaking the C–C bond [9, 15]. The solution to these problems is to use bi- or tri-metallic electrocatalysts combined with platinum. It is found that transition metals, such as Sn [16], Rh [17] and Pd [18] can enhance the catalytic activity for ethanol electrooxidation, and hence reduce the noble metal content [8, 19]. Recently, many

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authors [19–25] studied the methanol electrooxidation reaction on platinum and nickel particles co-deposited on carbon (Pt–Ni/C) with different compositions in acidic and alkaline media. They concluded that the electrocatalytic activity of Pt–Ni/C is more efficient for methanol oxidation than pure platinum. In addition, other authors [12, 15] have reported that both alcohol anodic oxidation and oxygen cathodic reduction kinetics in alkaline media are more facile than in acidic media. In the present work, we studied first the formation of Pt/C, Ni/C and Pt–Ni/C electrocatalysts by electrodeposition technique. Then, the electrocatalytic activity of these deposits on ethanol electrooxidation reaction in alkaline medium was investigated.

2 Experimental

Electrocatalysts were prepared by potentiostatic polarization of platinum (Pt), nickel, (Ni) or co-deposition of platinum and nickel (Pt–Ni) onto activated graphite (union carbide). All electrodepositions were made at a potentiostatic potential of -0.60 V versus saturated chloride silver electrode (Ag/AgCl, KCl_{sat}) from a solution containing appropriate amount of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Fluka) and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (Riedel-de-Haën). Before Pt and/or Ni electrodeposition, graphite electrode was subjected to mechanical treatment with metallurgical papers of different grades; then, it was cleaned with acetone to remove any organic impurities and finally rinsed with bidistilled water. In order to activate the graphite surface for further electrochemical reactions, this latter was firstly polarised at 1.8 V versus Ag/AgCl for 5 min, followed by a series of cyclic voltammetric scans (50 cycles) between the cathodic and the anodic limits in sulphuric acid (Fluka) with a scan rate of 50 mVs^{-1} . All electrochemical experiments were carried out in a conventional three-electrode glass cell using an EG & G Princeton Applied Research potentiostat/galvanostat model 273A controlled by Power Suite software. Solutions were purged with nitrogen for 15 min before measurements and a continuous flux of N_2 was maintained over solutions during experiments. The working electrodes were either, an activated graphite, platinum, nickel or platinum-nickel co-deposited on supported activated graphite. The reference electrode was (Ag/AgCl, KCl_{sat}), and a platinum wire served as the counter electrode. Electrochemical reactivities of the Pt/C, Ni/C and Pt–Ni/C electrodes were investigated in 1.0 M NaOH (Fluka) + 2.0 M ethanol (Riedel-de-Haën) aqueous solution by cyclic voltammetry with a scan rate of 50 mVs^{-1} . All potentials are expressed with respect to the Ag/AgCl reference electrode and all measurements were performed at room temperature.

3 Results and discussion

3.1 Electrochemical behaviour of Pt and Ni electrolytes on activated graphite in acidic medium

To determine platinum and nickel deposition potentials, the electrochemical behaviour of pure solvent (H_2SO_4) and electrolytes containing platinum and nickel salts were investigated by cyclic voltammetry. The characteristics of the obtained voltammograms are presented in Fig. 1. In order to better distinguish anodic and cathodic peaks in the potential range situated between -0.20 and 1.0 V, this part of the voltammograms is presented in the inset of Fig. 1. The voltammogram obtained in H_2SO_4 on activated graphite shows two peaks A1 and C1 in the potential range of $[0.30 \text{ and } 0.65]$ V corresponding to quinone/hydroquinone couple that is generated on graphite surface during electrochemical pre-treatment [26]. The shape of H_2PtCl_6 voltammogram is similar to those reported in the literature [27–30]. Three irreversible reduction peaks are observed: The first current peak C2 starting at 0.60 V can be assigned to the reduction of Pt^{+4} to Pt^{+2} , while C3 peak, located between 0.20 and 0.0 V is attributed to the reduction of Pt^{+4} or Pt^{+2} to Pt^0 . Finally, the C4 peak which is located between -0.05 and -0.18 V could be associated with the simultaneous electrodeposition of Pt and the discharge of H^+ ions. A disproportionation reaction of Pt^{+2} species into Pt^0 and Pt^{+4} species has also been included as a process taking place in the potential range of C2 peak. The anodic peak A2 which appears at 0.90 V corresponds to the oxidation of adsorbed oxygenated species on platinum surface already formed during the cathodic scan. The two peaks A3 and C5 correspond to the redox chloride couple [31]. The comparison between voltammograms recorded in sulphuric acid in the presence and in the absence of nickel sulphate indicates the deposition potential of nickel. It was suggested that the hydrogen evolution reaction and electrodeposition of Ni occur simultaneously from -0.60 V with a sharp increase in cathodic current [32]. The absence of anodic peak related to the oxidation of nickel indicates that the cathodic efficiency of nickel is very low. In the voltammogram related to the co-reduction of platinum and nickel ions, it is observed that hydrogen ions start discharge at -0.17 V due to the formation of platinum layers during cathodic scan. As a consequence of the ohmic behaviour, the nickel cathodic efficiency is lowered. This indicates that the deposition rate is slow, which favours the dispersed deposition of nickel particles.

3.2 Preparation of electrocatalysts

Before investigating deposition process, we have conducted a preliminary study to examine the electrochemical activation

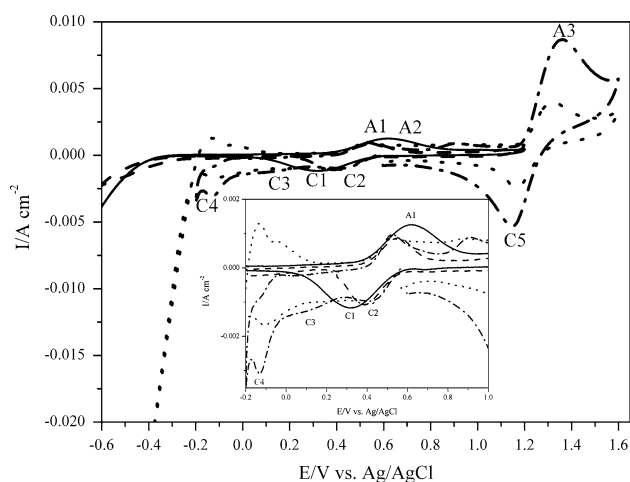


Fig. 1 Cyclic voltammograms on activated graphite electrodes in 1.0 M H_2SO_4 (solid line), 1.0 M H_2SO_4 + 128 mM NiSO_4 (continuous dashed line), 1.0 M H_2SO_4 + 8.0 mM H_2PtCl_6 (alternative dashed and dotted line), 1.0 M H_2SO_4 + 8.0 mM H_2PtCl_6 + 128 mM NiSO_4 (dotted line)

influence on graphite electrode behaviour. A cyclic voltammogram was run in 0.5 M KCl + 0.01 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution; Fig. 2. While the redox process behaviour of ferricyanide–ferrocyanide is similar on activated and inactivated graphite electrodes. The current density recorded with activated graphite is four times higher than that obtained with inactivated graphite. Hence, the activation of graphite may contribute to the acceleration of electronic exchange at the electrode interface.

Pt/C, Ni/C and Pt–Ni/C electrocatalysts were prepared electrochemically by the deposition on activated graphite of platinum, nickel and co-deposition of platinum and nickel from 16 mM H_2PtCl_6 , 128 mM NiSO_4 and 16 mM H_2PtCl_6 + 128 mM NiSO_4 solutions, respectively, in 1.0 M H_2SO_4 via a potentiostatic polarisation at -0.60 V.

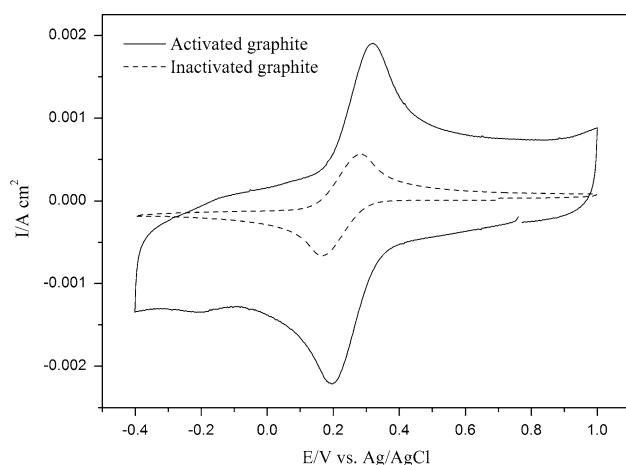
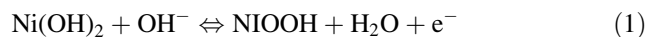


Fig. 2 Cyclic voltammogram of activated and inactivated graphite electrode in 0.5 M KCl 0.01 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution

Electrocatalysts' behaviours were studied by cyclic voltammetry in 1.0 M NaOH at 50 mVs^{-1} .

The voltammogram of Pt/C shows all platinum features in alkaline medium (Fig. 3), previously reported by some authors [4–6]. We can observe the hydrogen adsorption/desorption process which takes place in the potential region $[-0.92, -0.46]$ V. The current recorded after -0.46 V during the forward scan is due to the formation of the reversible (A5) and irreversible (A6) Pt hydroxide layers on the surface of the catalyst. During the reverse scan, a broad reduction peak (C6) is observed at -0.40 V, which represents the reduction of the Pt hydroxide layer. These findings confirm the formation of metallic platinum on activated graphite.

CV curve recorded on Ni/C electrode is shown in Fig. 4a. We observe an anodic peak (A7) at 0.43 V and the corresponding cathodic peak (C7) at 0.31 V due to the formation and dissolution of NiOOH according to the following reaction:



The high current recorded after the formation of NiOOH , at 0.55 V, is attributed to the oxygen evolution reaction. The cathodic peak (C8) at -0.38 V can be correlated to the reduction of nickel oxide species as shown by Fig. 4b. These features clearly indicate the deposition of nickel metal as reported by other authors [33–36], suggesting that the $\text{Ni}(\text{OH})_2$ film was successfully obtained on the surface of activated graphite electrode.

Figure 5a shows the cyclic voltammetric behaviour of the modified Pt–Ni/C electrode. When comparing voltammograms in Fig. 3, 4a, and 5a, the anodic and cathodic peaks that appear in these figures could be attributed to the deposition of both nickel and platinum. In fact, their own features are shown in Fig. 5a. We can distinguish three zones; the first one is related to the hydrogen adsorption/

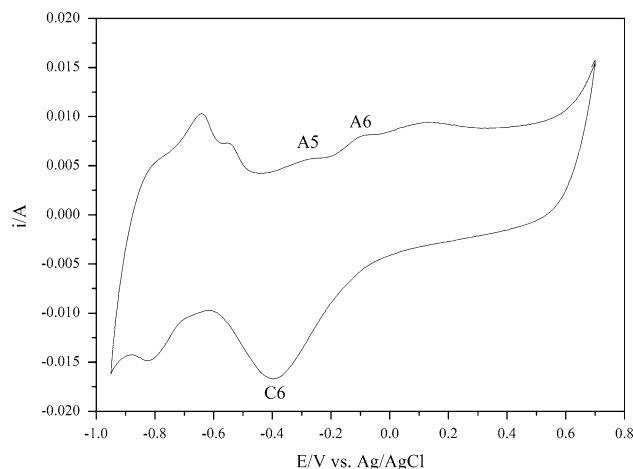


Fig. 3 Cyclic voltammogram of Pt/C electrode in 1.0 M NaOH solution

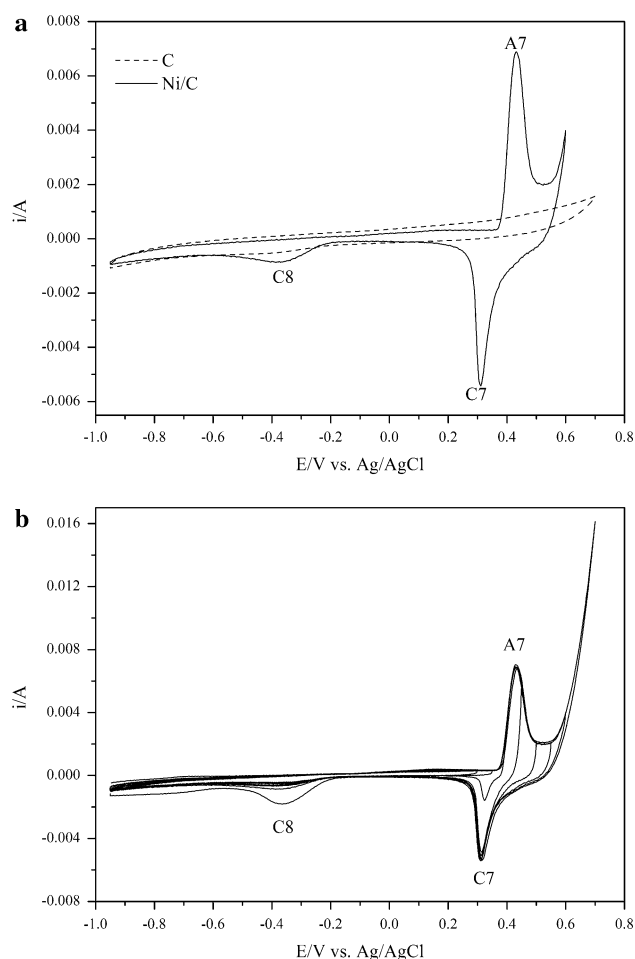


Fig. 4 Cyclic voltammogram of Ni/C and activated graphite electrodes in 1.0 M NaOH solution (a). Cyclic voltammogram of Ni/C electrode at different anodic reverse scans in 1.0 M NaOH solution (b)

desorption peaks on the platinum surface in the potential region $[-0.92, -0.46]$ V. Then, the platinum zone characterised by a cathodic peak related to the reduction of Pt hydroxide layer at -0.34 V (C6) and the formation of the reversible (A5) and irreversible (A6) Pt hydroxide layers. The third zone, where the pair of redox peaks (A7 and C7) is included, is attributed to the interconversion of $\text{Ni}(\text{OH})_2$ and NiOOH ; equation (1). The increase in the cathodic peak current related to the reduction of platinum oxide as function of the positive reverse scan, as shown in Fig 5b, indicates that the formation of the platinum oxide continues during all the anodic scans even after the formation of NiOOH . Also, we can see that the peak currents related to the proton reduction are not affected by varying the positive potential limit. This indicates that all platinum oxide is completely reduced during the cathodic scan.

Furthermore, the scan rate influence on the electrochemical behaviour of Ni oxide species on Pt–Ni/C corresponding to A7 and C7 was investigated by varying the

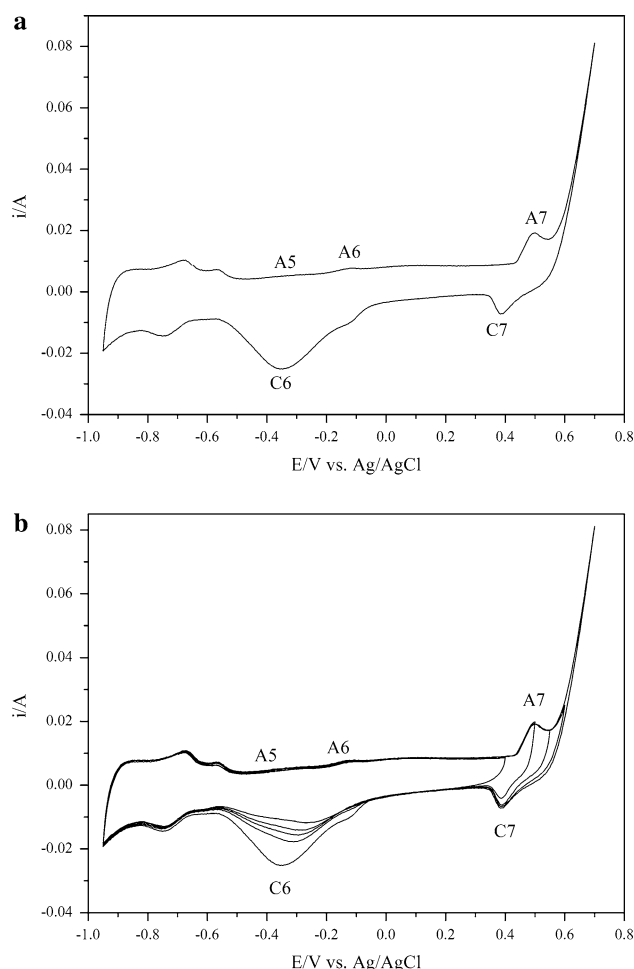


Fig. 5 Cyclic voltammogram of Pt–Ni/C electrode in 1.0 M NaOH solution (a). Cyclic voltammogram of Pt–Ni/C electrode in 1.0 M NaOH solution recorded with different positive potential limits (b)

scan rate, Fig. 6a. Anodic and cathodic peak currents are linearly dependent on the square root of the scan rate in all the studied scan rate range, Fig. 6b. According to the laws of the voltammetry technique, this relationship means that the electron transfer between $\text{Ni}(\text{OH})_2$ and NiOOH is a diffusion-controlled process. From the reaction (1), it is obvious that hydroxide ions are the diffusion species from and to electrode surface.

3.3 Ethanol electrooxidation on Pt/C, Ni/C and Pt–Ni/C

The electrocatalytic activities of the different electrocatalysts towards ethanol electrooxidation reaction in solution containing 1.0 M NaOH and 2.0 M ethanol at 50 mV s^{-1} scan rate were explored by cyclic voltammetry. The current densities of Pt/C and Pt–Ni/C are normalized to the active surface areas, which were calculated from the hydrogen adsorption charge as described by authors in Ref. [37]. As reported by other authors [10–13], the cyclic voltammograms for ethanol

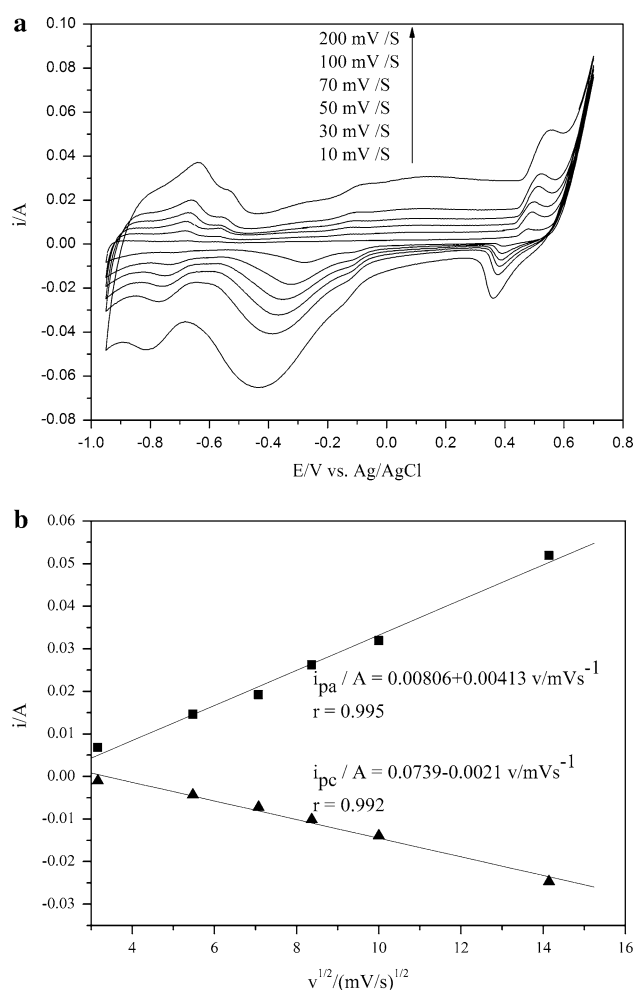


Fig. 6 Cyclic voltammogram of Pt–Ni/C electrode in 1.0 M NaOH solution at various scan rates (a). Dependence of the peak on the square root of scan rate (b)

electrooxidation on Pt/C (Fig. 7) shows a single anodic peak (A8) at 0.53 V in the forward scan. In the reverse scan, another anodic peak (A9) appears at −0.38 V. This latter can be explained by the oxidation of carbonaceous species on new free platinum surface after the platinum hydroxide reduction formed during the forward scan. The onset potential for ethanol electrooxidation coincides with the beginning of OH formation. We have also observed that the presence of ethanol changes the shape of the voltammogram in hydrogen adsorption/desorption region and indicates that ethanol is preferentially adsorbed on the surface of the electrode in this potential region and inhibits the adsorption of the hydrogen on the electrode surface. The inset in the Fig. 7 shows the CVs of activated graphite in 1.0 M NaOH solution with and without ethanol. It highlights that the contribution of activated graphite onto the oxidation of ethanol is negligible.

The cyclic voltammetric curve of Ni/C after the addition of 2.0 M ethanol (Fig. 8) is in good agreement with the published results [37–39]. The voltammogram is

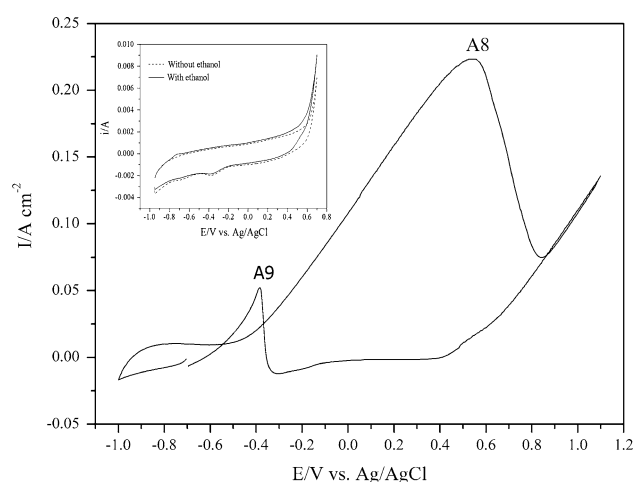
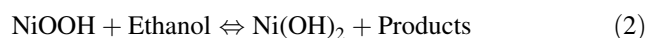


Fig. 7 Voltammetric behaviour of Pt/C electrode in 1.0 M NaOH solution in the presence of 2.0 M ethanol. The inset represents cyclic voltammograms of activated graphite in 1 M NaOH with (solid line) and without 2.0 M ethanol (dashed line)

characterized by two anodic oxidation peaks; the first one, A10, is obtained during the forward scan, while the second one, A11, is obtained during the reverse scan. The ethanol electrooxidation process starts with NiOOH formation at about 0.38 V. It was suggested that ethanol is oxidized on the nickel electrode through the following reaction [35]:



Comparison between Ni behaviour in the presence and in the absence of ethanol (Fig. 8) indicates that the consumption of NiOOH species during ethanol electrooxidation corroborate with the decrease in cathodic current at 0.31 V related to the reduction of NiOOH (C7).

The main objective of this study was to assess the electrocatalytic activity of the Pt–Ni/C towards the electrooxidation of ethanol. The obtained results were

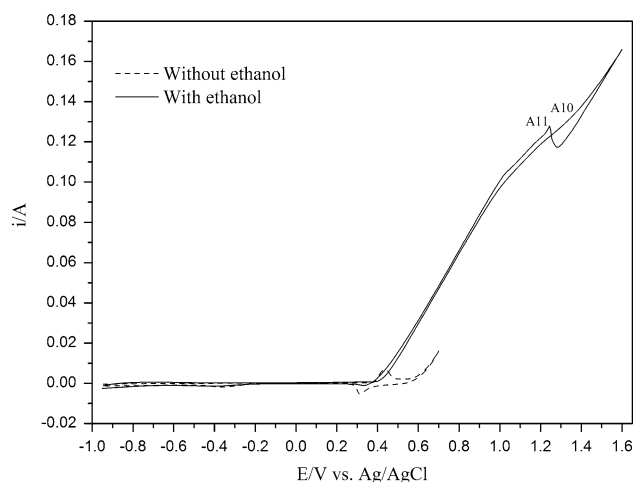


Fig. 8 Voltammetric behaviour of Ni/C electrodes in 1.0 M NaOH solution in the absence and in the presence of 2.0 M ethanol

compared with the Pt/C electrocatalyst (Fig. 9). It can be seen that the current density of ethanol electrooxidation on Pt–Ni/C electrode is about 2.3 times higher than that on Pt/C electrode. On the other hand, the electrooxidation onset potential at the Pt–Ni/C electrode is more negative than that observed for the Pt/C electrode. This indicates that the necessary energy for ethanol electrooxidation is lower in the case of Pt–Ni/C, which could be attributed to the synergetic role of nickel in platinum catalytic activity for ethanol electrooxidation on one hand and the modification of the electronic structure of Pt on the other hand. Moreover, the NiOOH formation on Pt–Ni/C starts from 0.42 V (Fig. 5a), which further promotes the electrooxidation of ethanol.

3.4 Study of electrocatalysts' stability

To characterize the stability of electrocatalysts, 50 cycles were applied on Pt–Ni/C and compared to that on Pt/C. The results are shown in Fig. 10. It can be seen that the peak current density decreases by 14 % on Pt–Ni/C, 25 % on Pt/C and 21 % on Ni/C if compared to that of the first cycle. This indicates that the presence of nickel improves the capability to remove adsorbed CO, as previously observed in the methanol electrooxidation [19]. This is attributed to the presence of oxygenated species on Ni sites formed at lower potentials in comparison with platinum. According to the bifunctional mechanism [19], these oxygenated species allow the oxidation of CO to CO₂ at lower potentials.

Long-term stabilities of electrocatalysts for ethanol electrooxidation have been investigated by means of chronoamperometry curves in 1.0 M NaOH solution containing

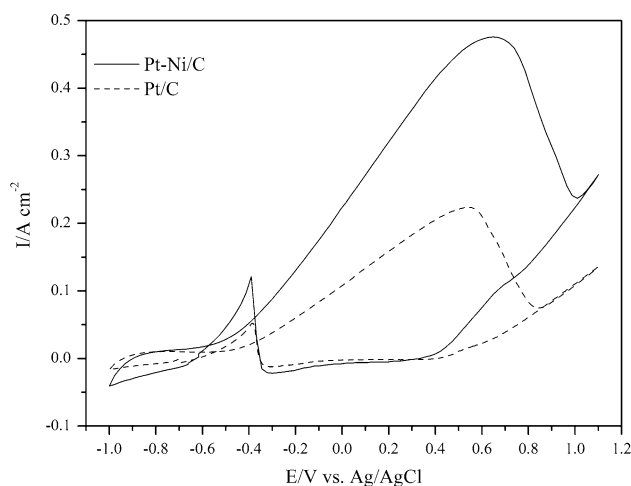


Fig. 9 Voltammetric behaviour of Pt/C and Pt–Ni/C electrodes in 1.0 M NaOH solution in the presence of 2.0 M ethanol

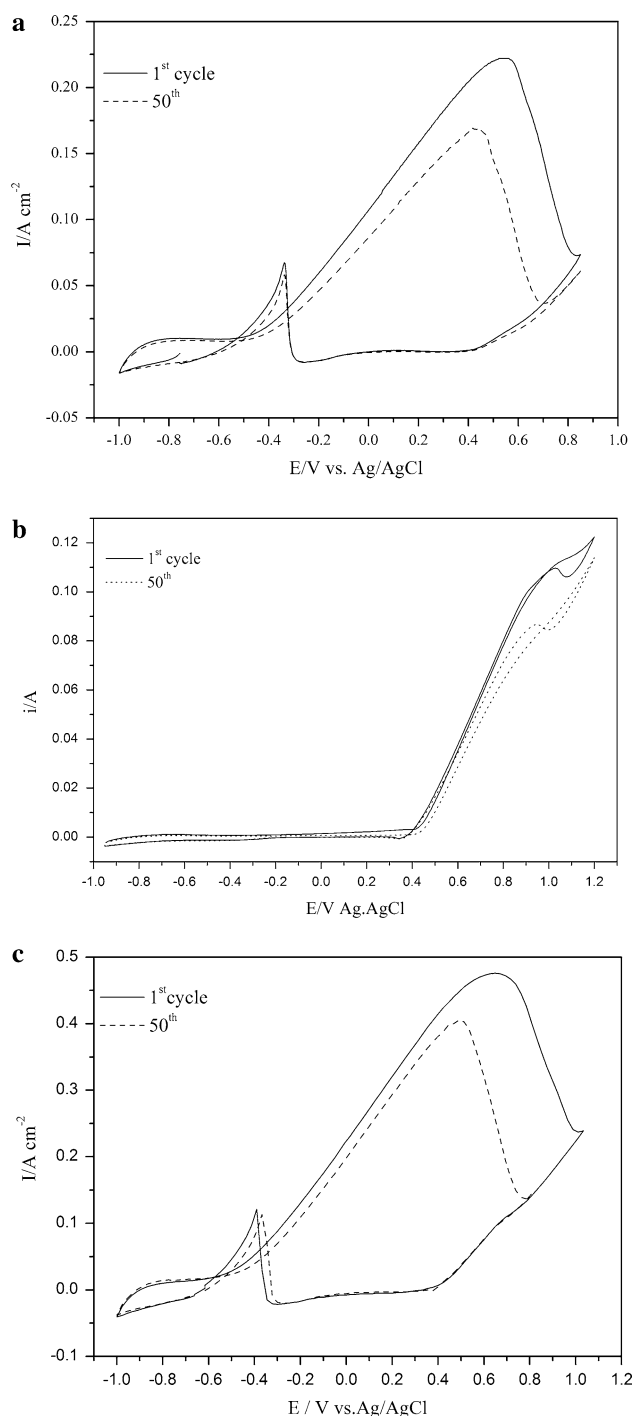


Fig. 10 Repeated cyclic voltammograms of ethanol electrooxidation on Pt/C (a), Ni/C (b) and Pt–Ni/C (c) at a scan rate of 50 mVs^{−1}

2.0 M ethanol at constant potential of 0.6 V (Fig. 11). The results show that the electrocatalytic advantage of Pt–Ni/C is maintained. This indicates that the Pt–Ni/C is more efficient and poisoning tolerant than the Pt/C, which is well consistent with the above cyclic voltammetric analysis.

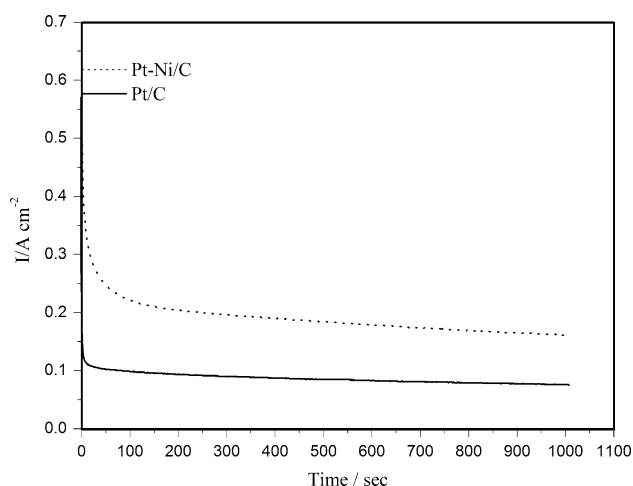


Fig. 11 Chronoamperograms of Pt–Ni/C (*dashed line*) and Pt/C (*solid line*) electrodes in 1.0 M NaOH solution in the presence of 2.0 M ethanol

4 Conclusion

Electrocatalytic activity of Pt/C, Ni/C and Pt–Ni/C electrocatalysts, prepared electrochemically by the reduction of inorganic precursor salts via potentiostatic polarisation, was explored for the electrooxidation of ethanol in alkaline medium. The investigation was conducted by cyclic voltammetry and chronoamperometry. We showed that ethanol electrooxidation on Ni/C occurs when NiOOH is formed. The performance of the Pt–Ni/C electrocatalyst for ethanol electrooxidation was found to be better than that of the Pt/C electrocatalyst due to the promoting effect of Ni. The tolerance performance to CO from intermediates of ethanol electrooxidation on the Pt–Ni/C is also better than that on Pt/C. In addition, the NiOOH formation shifts to lower potentials on Pt–Ni/C when compared to Ni/C which constitutes another promoting factor for ethanol electrooxidation. It can be concluded that nickel enhances the catalytic activity of platinum through nickel oxy-hydroxide (NiOOH) for ethanol electrooxidation.

As conclusion, the use of ethanol as fuel, platinum and nickel co-deposited on graphite electrode which is less expensive than platinum and the electrodeposition method which is recognized as simple and efficient, could contribute largely to the promotion of fuel cell application.

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